Lithium-Oxygen Battery Design and Predictions

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DOE merit review

June 10-12, 2019

Project ID# BAT-420

Overview

Timeline

- Start: 2018
- Finish: 2021
- 10 %

Barriers

- Barriers addressed
  - Cycle life
  - Capacity
  - Efficiency

Budget

- Total project funding
  - DOE share: $ 1500 K
  - Contractor 0
- FY 19: $ 500 K
- FY 20: $ 500 K
- FY 21: $ 500 K

Partners

- Interactions/ collaborations
  - B. Narayanan, University of Louisville
  - F. Khalili-Araghi, UIC
  - J. G. Wen, ANL
  - Robert Klie, UIC

Project Objectives and Relevance

- The objective of this work is to advance Li-O_2 battery concepts that operate in an air environment with long cycle life and high efficiency through novel design and predictions.
- A major goal of this work is to enable operation in an air environment and thus increase volumetric energy density needed for practical applications of Li-O_2 batteries
- The focus is on discovery of new combinations of electrolytes that can promote the cathode functionality of 2-dimensional transition metal dichalogenide (TMDC) catalysts that have high activity for oxygen reduction and evolution.
- Li-O_2 batteries are considered a potential alternative to Li-ion batteries for transportation applications due to their high theoretical specific energy
- In this project we will also explore other new concepts for batteries operating on chemical transformations principles that can have practical applications.

FY19 Milestones

Month/ Year	Milestones
Dec/18	Investigate electrolyte blends for lithium anode protection that can work with a MoS_2 cathode to extend cycle life and reduce charge overpotentials of Li-O_2 cells. Q1 (**Completed**)
Mar/19	Develop and assess additives for electrolytes that will work in concert with a MoS_2 cathode in oxygen atmosphere in Li-O_2 cells. Q2 (**Completed**)
Jun/19	Evaluate, using experiment and theory, properties of redox mediators for electrolyte blends to lower charge potentials for increased efficiency of Li-O_2 cells. Q3(**Initiated**)
Sep/19	Develop first generation of electrolytes that work in concert with a MoS_2 cathode for increased efficiency of Li-O_2 cells running in a realistic air environment Q4 (**Initiated**)

Strategy

- The strategy is to use cathode materials based on 2-dimensional transition metal dichalcogenides (TMDCs) that we have found to be among the best oxygen reduction and evolution catalysts* and have shown exceptional performance in Li-O_2 electrochemistry.
- These cathode materials will be the basis of our strategy to carry out systematic studies of electrolyte blends and additives that will reduce charge potentials and enable long cycle life.
- In the initial stages we will focus on establishing this strategy for an O_2 atmosphere and then extend to a realistic air atmosphere.
- The strategy will use integrated experimental/theoretical investigation to develop an understanding of the complex reaction mechanisms.
- We will also utilize a high throughput screening strategy based on experiment and theory to develop a large database of properties and outcomes of electrolyte combinations that can be analyzed using artificial intelligence to predict electrolytes and additives that will have the best performance.

* Salehi-Khojin, Curtiss, et al Adv.Mater.2019, 31, 1804453

Experimental and computational methods

Synthesis of cathode materials

Chemical Vapor Transport method for the synthesis of bulk cathode materials; liquid phase exfoliation technique to produce nanostructured cathode materials

Characterization and Testing

DLS, AFM, TEM imaging, EDXXPS, Raman, XRD, SEM, DEMS imaging, impedance measurements, cyclic voltammetry (CV), high throughput screening, charge-discharge cycling experiments in Swagelok systems

Computation

Density functional theory (DFT), ab initio molecular dynamics (AIMD), classical molecular dynamics (CMD), periodic and cluster calculations, high throughput screening, machine learning and artificial intelligence for optimizing electrolyte/catalyst synergies and CMD potential development

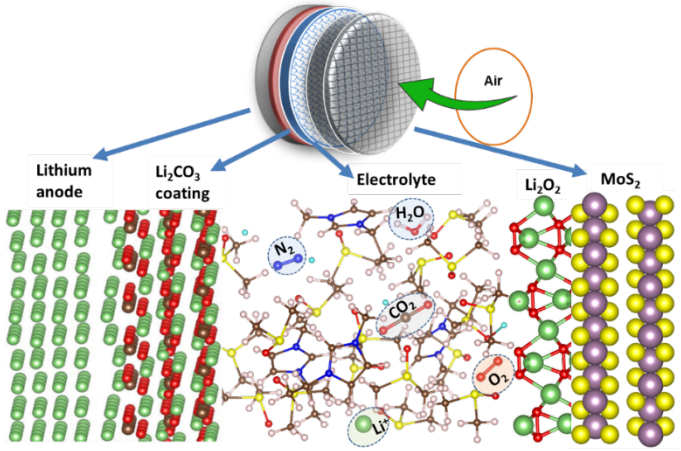
Technical Accomplishments

The first step in our strategy to develop a high performance Li-O_2 battery that operates in an air environment has been completed

- Established a new electrolyte combination that works to protect the Li anode and reduce charge potentiasl at the same time for a Li-O_2 battery in an O_2 environment
- This was done by using a high concentration of LiI redox mediator for the first time to efficiently decompose the Li_2O_2 product with significantly reduced charge potential
- Computational studies were used to establish insight into how the electrolyte combination operates

A MoS_2 catalyst that works well in the Li-O_2 battery was found to also reversibly discharge and charge Li_2CO_3 in a Li-CO_2 battery for many cycles

Background for this work: "Long Cycle Life Li-O_2 Batteries that can Operate in an Air Atmosphere", L. A. Curtiss, A. Salehi-Khojin, A. Ngo, et al Nature, *555*, 502-507 (2018)



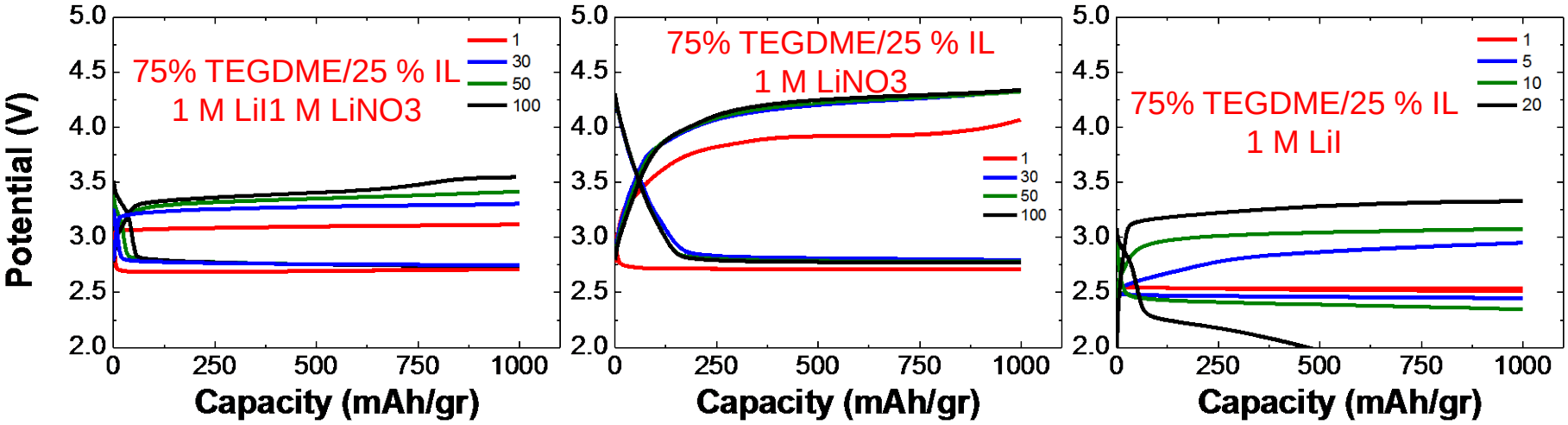
Performance

- Cycle life: 550 cycles without capacity fade
- Capacity of 500 mAh/g
- High charge overpotential with cycling

- Coated the lithium anode with a thin layer of lithium carbonate that selectively allowed lithium ions through and prevented unwanted components such as nitrogen from reaching the anode
- The cathode used a molybdenum disulfide catalyst with high activity for OER and ORR
- A hybrid electrolyte made of ionic liquid and dimethyl sulfoxide that helped facilitate the ORR and minimize lithium reactions with other components in the air

- **Provides basis for making advances in Li-O_2 batteries that operate in air with lower charge overpotentials and larger capacities, while maintaining cyclability**

Accomplishment: Established a new electrolyte combination that works to protect the Li anode and reduce charge potentials at the same time for a Li-O_2 battery in an O_2 environment



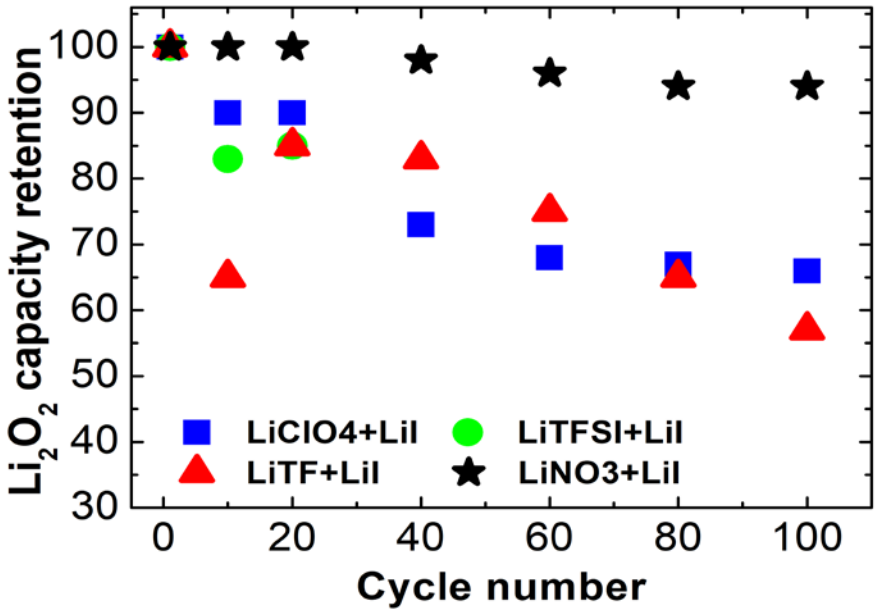
Long cycle life, low charge potential

Long cycle life, high charge potential

Short cycle life, low charge potential

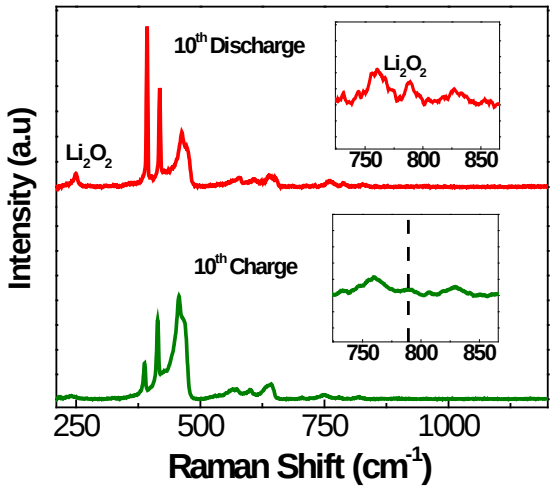
- First results on using high concentration of LiI redox mediator along with $LiNO_3$ to efficiently decompose the Li_2O_2 product with significantly reduced charge potential and long cycle life
- A new approach to design advanced Li-O2 batteries with large capacity (increased Li_2O_2 product) and good energy efficiency (reduced polarization gap)

Voltage profiles reveal a unique synergy among TEGDME/IL hybrid electrolyte, $LiNO_3$ salt and LiI redox mediator

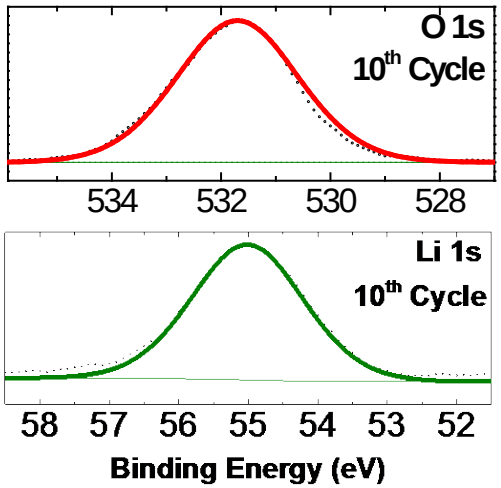


- A novel electrolyte chemistry leading to increased Li_2O_2 capacity retention e.g., ~96% after 100 charge-discharge cycles compared to other salt combinations

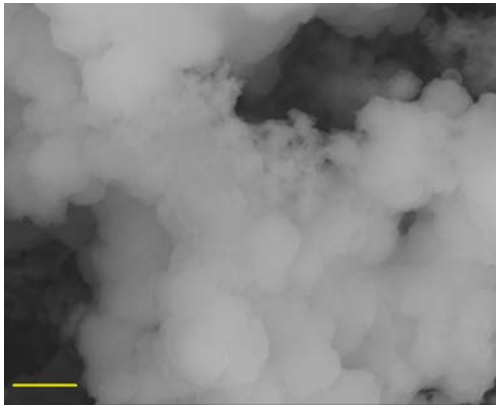
Characterization of cathode: Raman, XPS and SEM results for discharge and charge processes



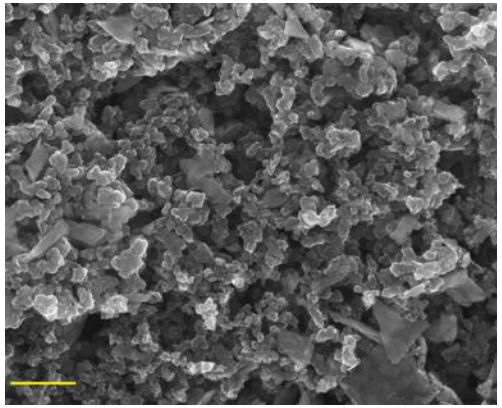
Raman results of cathode after charge and discharge



XPS results of cathode after discharge



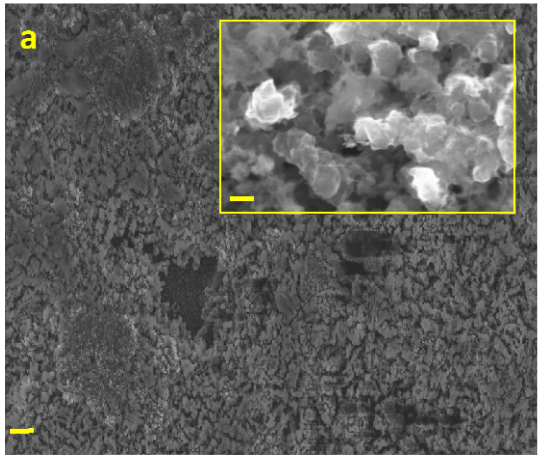
SEM image of cathode after discharge



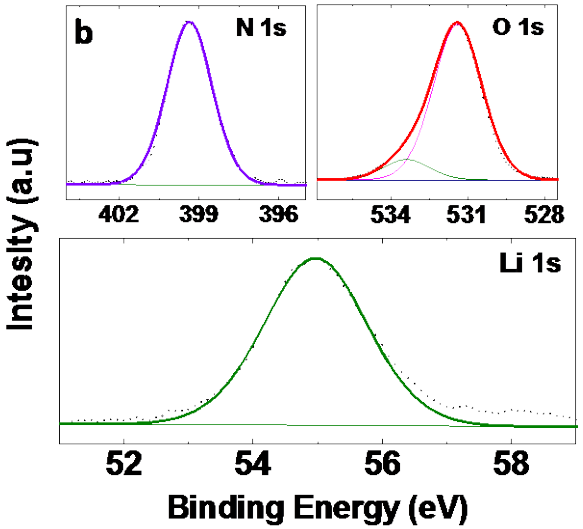
SEM image of cathode after charge

- Producing Li_2O_2 products rather than LiOH or Li_2CO_3 using high concentration of LiI redox mediator
- Reversible formation and decomposition of Li_2O_2 during the battery operation at relatively high current density of 500 mA/gr.

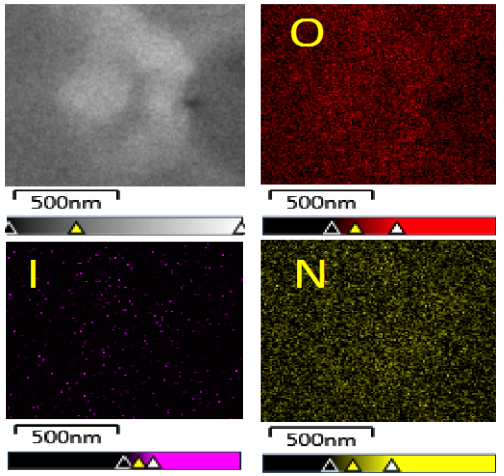
Characterization of Li anode: SEM, XPS and EDX results



SEM image of anode after 10 cycles



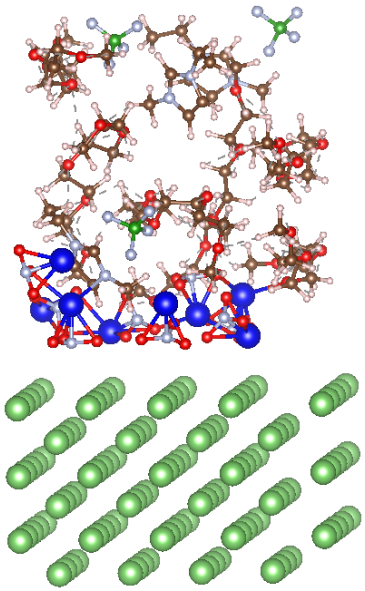
XPS results of anode after 10 cycles



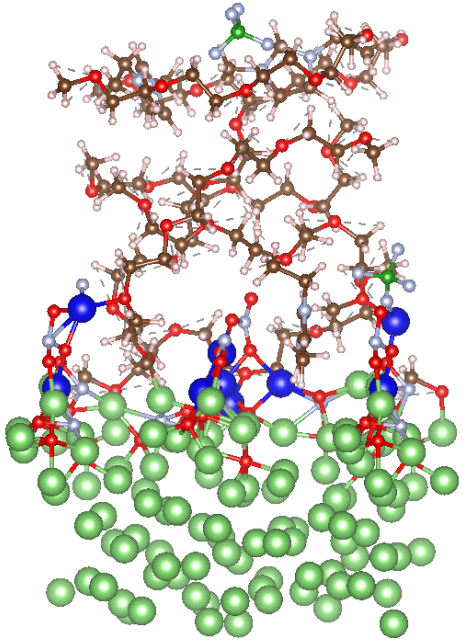
EDX results of anode after 10 cycles

- Relatively homogenous SEI layer composed of Li, O and N on the top of the Li anode surface
- Further TEM and EELS characterizations are underway.

AIMD simulation of eight $LiNO_3$ molecules in a TEGDME/IL electrolyte on a Li(100) surface



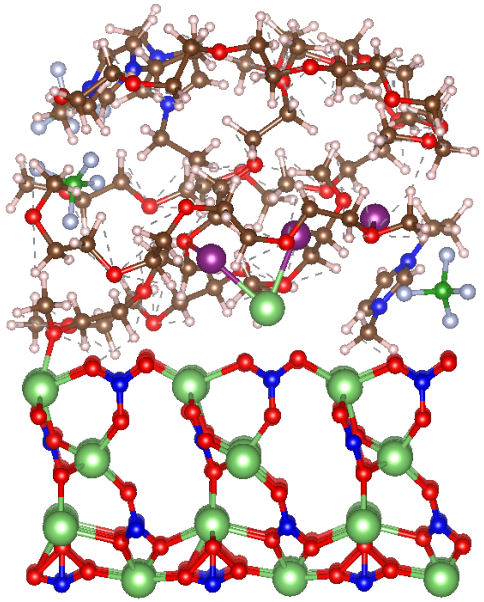
Initial configuration



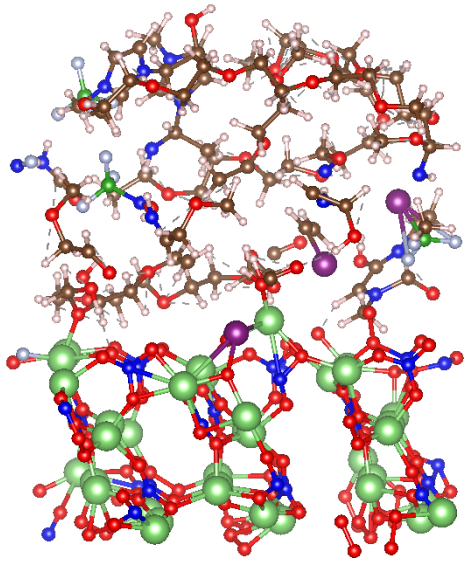
Optimized configuration

- Simulations show that $LiNO_3$ salts will react with a Li surface. Subsequent electrochemical reactions will modify this initial SEI. Studies are underway to identify the resulting SEI.

AIMD simulation of $LiNO_3$ interface (as a model for the SEI) with TEGDME/IL electrolyte with a LiI_3 added to the electrolyte



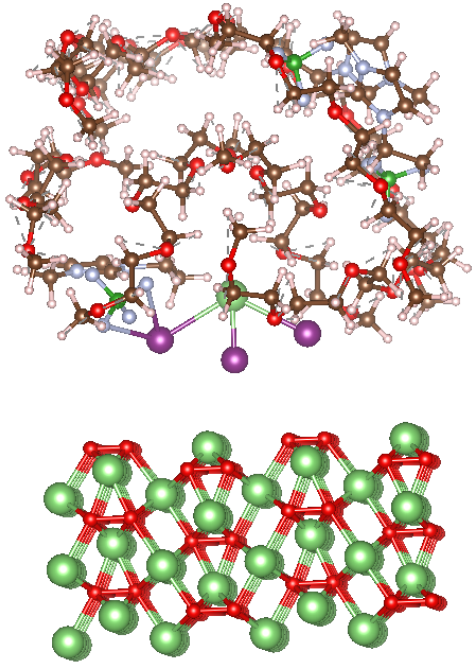
Initial configuration



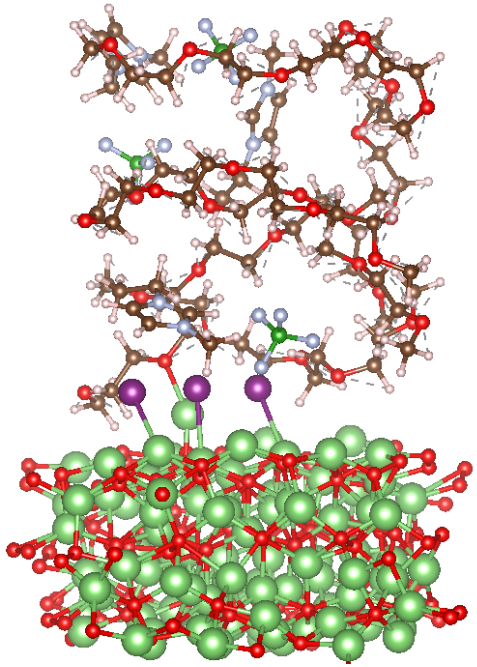
Optimized configuration

- We studied several surfaces of $LiNO_3$ and found that the (101) $LiNO_3$ surface with O termination has the lowest surface energy
- When a LiI_3 molecule was added into mixed electrolyte on (101) $LiNO_3$ surface calculations show that LiI_3 can not enter SEI and reach the Li anode showing how the SEI can protect the anode

AIMD simulation of TEGDME/IL electrolyte on a Li_2O_2 surface with an redox mediator, LiI_3, in the electrolyte



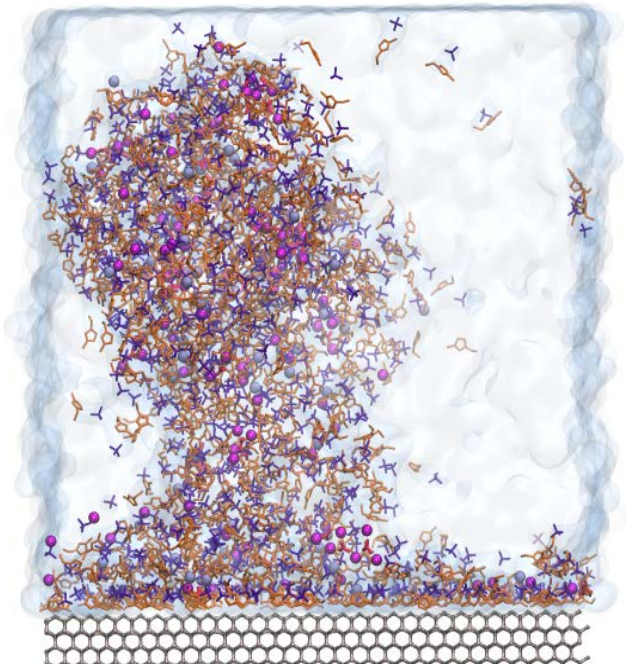
Initial configuration



Optimized configuration

- The simulation shows that the LiI_3 molecule reacts with the Li_2O_2 surface to form three LiI units on the surface. This is the first step by which LiI_3 promotes decomposition of Li_2O_2. Current calculations are underway to investigate the abstraction (barrier) of Li from the surface from the optimized configuration on the right.

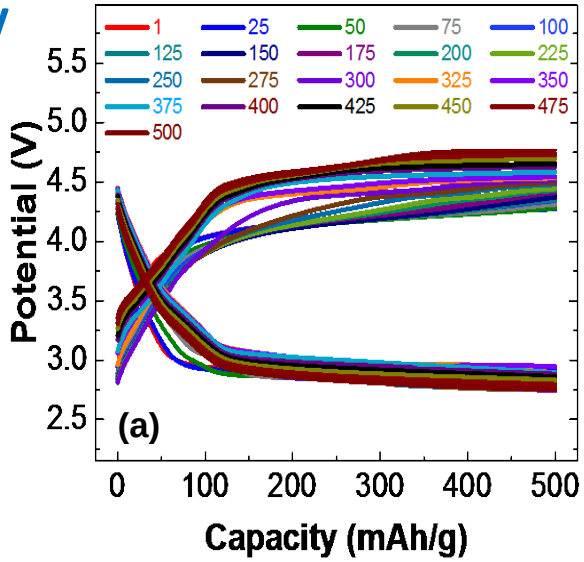
Classical Molecular Dynamics (CMD) simulation of the electrolyte/MoS_2 System under electric potential



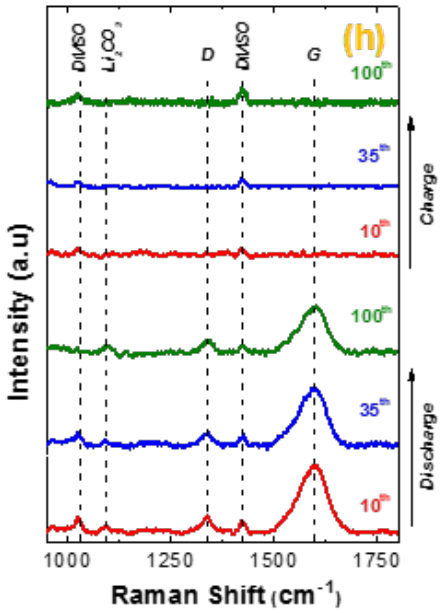
All-atom MD simulation of a system containing TEGDME, $EMIM^+$, BF_4^-, $LiNO_3$, and LiI (115K atoms). (a) Initial and (b) final distribution of the components in solution show formation of two separate domains for TEGDME or TEGDME and ions after 550ns. (c) Domain formation critically slows down the diffusion rate of ions, including Li^+ (shown in magenta) in solution and confines them within the domains. Four common clusters of Li^+/TEGDME/BF_4^-, Li^+/TEGDME/BF_4^-/NO_3^-, Li^+/BF_4^-/NO_3^-/I, and Li^+/BF_4^- are shown.

- All-atom MD simulations of the system shows domain formation of electrolyte components for the first time that confines diffusion of ions inside solution.

Accomplishment: Demonstrated that MoS_2 catalyst can reversibly discharge and charge Li_2CO_3 in a Li-CO_2 battery in addition to working well in a Li-O_2 battery



Electrochemical performance of Li-CO_2 battery using MoS_2 as a cathode and a hybrid electrolyte (IL/DMSO) with 0.1M LiTFSI. Discharge and charge voltage profile up to 500 cycles with the capacity of 500 mAh/g per cycle.



Raman spectra showing Li_2CO_3 and C from discharge in a Li-CO_2 cell and disappearance after charge for various cycles..

- The first fully reversible long cycle life rechargeable Li-CO_2 battery with carbon neutrality
- These results show that electrochemical transformation of covalent carbon-oxygen bonds can be used for energy storage.

Response to last year reviewer's comments

No comments from last year.

Proposed Future Work

- Based on our initial success, we will develop Li-O_2 batteries that can operate in a realistic air atmosphere with a low charge potential and a long cycle life.
- Two complementary strategies will be used.
  - The first will be systematic studies of electrolyte blends and additives to find ones that protect the Li anode, are stable, and enable easy decomposition of the discharge product while being able to operate in air
  - The second will be a high throughput screening strategy based on experiment and theory to develop a large database of properties and outcomes of electrolyte combinations that can be analyzed using artificial intelligence to predict electrolytes and additives that will have the best performance.
- In addition, to low charge potentials and long cycle life we will also extend the studies to obtain larger capacities to enable large energy densities.

Remaining Challenges and Barriers

- This is a project that just started and its major challenge remains the discovery of electrolytes that work in combination with transition metal dichalgonide catalysts that can operate effectively in an air environment.
- A second major challenge is to assess and optimize the Li-O_2 lab scale batteries to be able to have practical applications outside the lab, which will be a future goal for this work.

Collaborations with other institutions and companies

- Badri Narayanan (University of Louisville)
  - Machine learning
- Robert Klie (UIC)
  - TEM studies of SEI of Li anodes and discharge product on cathodes
- J. G. Wen (ANL)
  - TEM studies of SEI of Li anodes and discharge product on cathodes
- F. Khalili-Araghi, (UIC)
  - Classical molecular dynamics simulations of bulk electrolytes

Summary

The first step in our strategy to develop a high performance Li-O_2 battery that operates in an air environment has been completed

- Established a new electrolyte combination that works to protect the Li anode and reduce charge potential at the same time for a Li-O_2 battery in an O_2 environment
- This was done by using a high concentration of LiI redox mediator for the first time to efficiently decompose the Li_2O_2 product with significantly reduced charge potential
- Computational studies were used to establish insight into how the electrolyte combination operates

A MoS_2 catalyst that works well in the Li-O_2 battery was found to also reversibly discharge and charge Li_2CO_3 in a Li-CO_2 battery for many cycles